

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09C 1/28, 3/06	A1	(11) International Publication Number: WO 93/10193 (43) International Publication Date: 27 May 1993 (27.05.93)
(21) International Application Number: PCT/US92/08462 (22) International Filing Date: 2 October 1992 (02.10.92) (30) Priority data: 791,821 13 November 1991 (13.11.91) US (60) Parent Application or Grant (63) Related by Continuation US 791,821 (CIP) Filed on 13 November 1991 (13.11.91) (71) Applicant (for all designated States except US): ENGELHARD CORPORATION [US/US]; 101 Wood Avenue, Iselin, NJ 08830 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : WILLIS, Mitchell, J. [US/US]; 174 Clisby Place, Macon, GA 31204 (US). CANAVAN, Patrick, D. [US/US]; 41 Eastern Parkway, Brooklyn, NY 11238 (US). ALLEN, Fred, Mitchell [US/US]; 1 Hart Court, East Windsor, NJ 08520 (US). LAMPERT, Jordan, K. [US/US]; 31 Hickory Street, Metuchen, Middlesex, NJ 08840 (US). (74) Agents: MILLER, Stephen, I. et al.; Engelhard Corporation, 101 Wood Avenue, Iselin, NJ 08830 (US). (81) Designated States: FI, JP, NO, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: PAPER COATING KAOLIN PIGMENTS THEIR PREPARATION AND USE (57) Abstract Paper coating pigments comprising mechanically delaminated kaolin particles. The pigments possess the opacification, smoothness and printability advantages of conventional delaminated kaolin pigments but have desirably low viscosity and gloss not characteristic of conventional delaminated kaolin pigments. Crude kaolins of specified physical characteristics for production of these pigments by controlled delamination.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

- 1 -

5

PAPER COATING KAOLIN PIGMENTS
THEIR PREPARATION AND USE

10 This invention relates to novel mechanically delaminated kaolin clay pigments especially useful for coating lightweight printed paper. In particular, the invention relates to delaminated kaolin coating pigments which possess a unique combination of desirable properties not possessed by other kaolin pigments.

15 Kaolin clay pigments are obtained from kaolin crudes. The crudes contain kaolin particles, oversize (grit) and fine and coarse particle size impurities. Some impurities (e.g., fine ferruginous or titaniferous impurities) impart undesirable color to the clay. Other
20 impurities have an undesirable effect on the rheology of the kaolin.

The kaolin portion of kaolin crudes is "polydisperse" in the sense that the particles occur over a range of sizes and shapes. Thus, a kaolin crude will
25 not contain particles of a single size, such as, for example, particles all of which are 2 micrometers. Typically a degrittied kaolin crude will contain particles ranging in size from sub-micron or colloidal to particles
20 micrometers or larger.

30 Kaolins from different ores, or even from different zones in the same deposit, can vary widely in the content of impurities, particle size distribution, and the morphology of the kaolin particles. In general, kaolin

- 2 -

particles finer than about 2 micrometers are composed of individual platelets, and particles larger than about 2 micrometers are composed of stacks or booklets of finer particles. Particle sizes of kaolins are conventionally determined by sedimentation using Stokes law to convert settling rates to particle size distribution, and assume a spherical particle shape for the kaolin particles. Hence, the use of the conventional term "equivalent spherical diameter (e.s.d.)" to designate particle size.

Kaolin clay pigments are widely used to coat and to fill paper products and they are also used as functional fillers in paints and plastics. Such pigments are available in a large number grades, the selection of which by the user is determined by price and performance. It was formerly the practice simply to use relatively coarse kaolins to fill papers and to employ finer grades of kaolin to coat paper. In paper the coarser kaolin fillers functioned primarily as pulp extenders. When used to coat paper, the finer kaolin pigments improved opacity and provided a smooth, ink-receptive surface and gloss which improved print quality and aesthetic appearance.

It has long been recognized in the industrial minerals industry that mechanical delamination of kaolin stacks present in the coarse particle size fractions of many kaolin crudes provides kaolin pigments with improved opacification as well as enhanced smoothness in paper coating. See, for example U.S. 3,171,718, Gunn et al.

During mechanical delamination, large kaolin particles are disaggregated into smaller particles having a higher aspect ratio, principally by parting clay crystals along basal cleavages. It has also been recognized that a relative narrowing of the particle size

- 3 -

distribution of mechanically delaminated as well as non-delaminated kaolin particles results in pigments providing improved opacity and smoothness to paper along with improved printability. Such pigments are disclosed as being especially advantageous when used in the manufacture of lightweight coated paper for rotogravure printing (see GB 2,058,734). The characteristics of delaminated pigments are particularly beneficial in the coating of ground wood - containing paper basestock, which is typically of substantially lower uncoated sheet brightness and of rougher surface than chemical wood-free basestock.

Delaminated pigments in clay-water slurries and in paper coating color formulations have, however, had substantially poorer high shear rheological characteristics (higher viscosity) than undelaminated pigments. Superior rheology in coating color formulations permits the paper coating equipment to run at higher speeds (which directly increases the productivity of existing coating equipment) or permits the formulation of coating colors at higher solids (thus reducing drying time and hence increasing the efficiency of drying equipment). Thus, with the use of conventional delaminated pigments, papermakers must balance the tradeoff between paper opacification (quality) and efficiency of production (productivity).

Coating color viscosity is a key issue with paper coaters facing capacity constraints. A clay-water slurry that has equivalent viscosity to a comparable slurry at only 2 - 3% higher pigment solids represents an improvement of significant commercial importance.

Generally, paper makers seek to use clay coating pigments capable of forming clay-water slurries at 67-70%

solids which have a low shear viscosity below 1000 cp, preferably below 500 cp, when measured by the Brookfield Viscometer at 20 rpm. High shear viscosity for these slurries should be such that they are no more viscous than a slurry having a Hercules endpoint viscosity at 16 X 10⁵ dyne-cm of 500 rpm, preferably 800 rpm, using the "A" bob. Those skilled in the art are aware that when using the Hercules Viscometer and measuring endpoints of 1100 rpm or higher, viscosity is reported in units of dyne-cm at 1100 rpm. It is conventional to use the abbreviated term "dyne". A "2 dyne" clay slurry is less viscous than a "9 dyne clay" slurry at a given solids level.

Kaolin pigments produced by mechanical delamination are currently commercially made and marketed as delaminated pigments by various producers with processing facilities located in Georgia and South Carolina, using as raw material sources the Cretaceous and Tertiary kaolin deposits of the region. However, none of the commercially available delaminated kaolin pigments have the unique desirable combination of high opacification and the low viscosity characteristic of some undelaminated pigments.

SUMMARY OF THE INVENTION

We have developed, and the invention provides, kaolin pigments which possess the opacification, smoothness, and printability advantages of delaminated kaolin pigment with narrow particle size distribution and with high and low shear viscosities that provide paper-makers with productivity enhancements. Kaolin pigments according to the invention can be especially useful for high-speed coating of lightweight ground wood paper.

- 5 -

5 We have also ascertained the characteristics for kaolin
crudes which result, on delamination of the crudes, in kaolin
pigments having such improvement of combined properties. We have
also identified specific kaolin crudes, available for example from
10 Georgia, USA, the Rio Capim area of Para, Brazil and Manaus,
Amazonas, Brazil, which are capable of providing delaminated kaolin
pigments having both desirable low viscosity not normally
associated with delaminated pigments and desirable optical
properties of opacification normally associated with coarse
15 particle size delaminated kaolin pigments, and sometimes also
desirable optical properties of gloss not normally associated with
delaminated pigments.

15 The present invention provides kaolin pigments comprising
delaminated kaolin particles and possessing the following
distinguishing combination of properties or characteristics:

Particle Size (weight percent finer than stated
equivalent spherical diameter,
e.s.d., as measured by Sedigraph)

20 At least 95% finer than 10 micrometers
37% or less finer than 0.5 micrometers
12% or less finer than 0.2 micrometers

Median particle size: at least 0.70 micrometers

The ratio of $\frac{\% \text{ finer than } 2.0 \text{ microns}}{\% \text{ finer than } 0.5 \text{ microns}} > 2.0$

25 Surface Area of 12.5 m²/gm or less (BET method
using N₂ as adsorbate)

Viscosity

Brookfield viscosity, measured at 20 rpm
[#2 spindle] and 67-68% solids: 175 cp or less

30 and, most preferably, Brookfield viscosity, measured
at 20 rpm [#2 spindle] and at 100 rpm [#2 spindle]

- 6 -

at 72% solids: 300 cp or less

Hercules viscosity, measured at 1100 rpm [A-bob]
and 67-68% solids: dyne endpoint

Opacity and gloss (as measured by black glass)

- 5 scatter coefficient at 457 nm: $\geq 100.0 \text{ m}^2/\text{Kg}$
scatter coefficient at 577 nm: $\geq 80.0 \text{ m}^2/\text{Kg}$
gloss: preferably at least 75%

- Other aspects of the invention comprise aqueous
paper coating compositions containing the pigment of the
10 invention with organic binder, and paper webs coated
with kaolin pigments of the invention.

- The invention further provides a method of making a
hydrous kaolin pigment which comprises delaminating degrittied minus
325 mesh (i.e. minus 0.044mm) kaolin crude having the following
15 characteristics:

(1) Particle Size (e.s.d. as determined by Sedigraph)

- (a) % less than 2 microns: 40 - 65%
% less than 0.2 microns : $\leq 12\%$, preferably $\leq 5\%$
(b) ratio % less than 2 microns : > 2.1
20 % less than 0.5 microns

(2) Surface Area: $12.0 \text{ m}^2/\text{gm}$ or less (BET method using N_2 as
adsorbate).

(3) Structural Order

- (a) Hinckley Index: ≥ 0.90 , indicating a high degree of
25 overall structural order
(b) C-axis crystal coherence - Full-Width-Half-Maximum
measure of (001) peaks -
FWHM (001) ≤ 0.26 , indicating thick, well-formed,
coherent crystallites - the basic diffracting unit of the
crystal structure (Plancon et al, 1988)

- 7 -

(4) Cation Exchange Capacity - measured by Na^+ adsorption at pH 4.0 on non-dispersed minus 325 mesh crude: ≤ 0.05 microequivalents/ m^2 .

5 Delaminated kaolin pigments according to the invention have been produced from Rio Capim and Manaus crudes, and these crudes and appropriate crudes from Georgia and elsewhere can be used in the methods according to the invention. The kaolin crude of the above characteristics used as a bulk feed in the method of the invention may be a whole crude or a fractionated crude or a
10 mixture of whole or fractionated crudes or both. It is a feature of this invention to terminate delamination when the predominant proportion of booklets have been parted by mechanically induced shearing along basal (001) cleavages into discrete platelets, but prior to onset of undesired significant attrition of the platelets.
15 The point at which to terminate delamination is generally determined by calculating the rate of change in the particle size distribution at particular particle size control points versus residence time in the delaminator, and ceasing delamination when the rate of change approaches zero, and/or when an increase in the
20 percentage of very fine particles (e.g. less than .3 microns) is noted. The said particle size control points could for example be one or more or all of those used above in definition of pigment according to the invention (10, 0.5 and 0.2 micrometers), or particle sizes from a similar range.

25

DESCRIPTION OF PREFERRED EMBODIMENTS

The following chart summarizes the physical characteristics of seven coarse kaolin crudes, including crudes that meet the criteria and will make products of the invention as well as those that fail to meet the criteria or make products of the invention.

5

Crudes 1, 4, 5, 6 and 7 are kaolins sampled from various kaolin deposits in central Georgia, USA, and crudes 2 and 3 are kaolin crudes from the Amazon region of Brazil. Crudes 1, 2 and 3 satisfy all of the criteria of required physical characteristics for use in the methods according to the invention; products of the invention have been made from crudes 2 and 3.

10

In this chart, the viscosity characteristics are proxied by fluidity which denotes maximum solids achieved at optimum dispersion with a Brookfield value of 300 cps. All values reported are for de-gritted, minus 325 mesh crudes with the exception of the structural order characteristics, which are measured on whole crude.

CRUDE	1	2	3	4	5	6	7
Fluidity (solids @ 300 cps)	77.9	76.6	73.6	68.7	67.4	62.5	64.1
<u>Surface Area</u> (BET, N ₂)							
SA (m ² /g)	9.3	8.5	10.8	11.9	16.4	14.6	13.2
<u>Particle Size Distribution</u>							
5µm (% finer)	73.3	76.0	72.0	75.5	76.9	72.9	60.9
2µm (% finer)	54.2	55.0	51.0	54.2	56.9	61.2	43.2
1µm (% finer)	39.5	40.4	32.0	42.4	43.6	48.5	31.8
0.5µm (% finer)	16.6	23.3	10.5	25.3	28.1	31.7	20.7
0.2µm (% finer)	2.4	10.3	0.0	6.3	8.4	11.1	7.0
Ratio $\frac{\% -2\mu\text{m}}{\% -.5\mu\text{m}}$	3.26	2.36	4.86	2.14	2.0	1.9	2.1
<u>Structural Order</u>							
Hinckley Index	1.07	1.06	1.05	.62		.68	.55
FWHM "001"	.25	.25	.22	.29		.25	.30
<u>Cation Exchange Capacity</u> (microequivalents/m ²)							
pH 4	.33			.36	.30	1.00	.39

- 9 -

A typical prior commercial delaminated pigment from a Georgia producer will have the following characteristics:

	<u>Particle Size</u>	79% finer than	2 micrometers
5	<u>Distribution</u>	63% finer than	1 micrometers
	(weight % finer	43% finer than	0.5 micrometers
	than e.s.d.)	16% finer than	0.2 micrometers
	Ratio	<u>% finer than 2.0 micrometers</u>	<2.0
		<u>% finer than 0.5 micrometers</u>	
10	Median Particle Size: less than 0.65 micrometers		
	<u>Surface Area</u>	15.0 m ² /g	

- 10 -

Viscosity

Brookfield: 275 cp @ 20 rpm @ 68% solids
>300 cp @ 20 rpm @ 68 - 69% solids

5 Hercules endpoint: 600 rpm @ 68% solids

Black glass:

scatter coefficient at 457 nm: 100 m²/Kg
scatter coefficient at 577 nm: 75 m²/Kg
gloss: 68%

10 Some commercially available kaolin pigments marketed
as delaminated pigments will exhibit better viscosity
than is indicated above. These pigments may have dyne-
endpoint high shear viscosity at 68% solids. However,
15 these particular pigments will be finer than the products
of the invention and the above typical delaminated
pigment, as measured by a higher surface area and the
higher weight percentage of kaolin particles finer than
the 0.5 micrometers and 0.2 micrometers control points.
20 While the presence of fine kaolin particles improves the
high shear viscosity of delaminated kaolin pigments, the
presence of fines concomitantly reduces the scattering
efficiency and opacification of the pigments, as
quantified by a reduction in the black glass scatter
25 coefficients of the "good" viscosity pigment below those
values for products of the invention. For example, the
"best" viscosity, commercially available delaminated
pigment tested had the following characteristics:

Particle Size

30 (weight % finer than e.s.d.)	98% finer than 5.0 micrometers 81% finer than 2.0 micrometers 67% finer than 1.0 micrometers 50% finer than 0.5 micrometers 21% finer than 0.2 micrometers
------------------------------------	--

35

- 11 -

Median Particle Size 0.50 micrometers

Ratio: $\frac{\% \text{ finer than } 2.0 \text{ micrometers}}{\% \text{ finer than } 0.5 \text{ micrometers}} = 1.6$

Surface Area 16.9 m²/g

Viscosity

Hercules viscosity, measured at 1100 rpm (A bob)
and 68% solids: 15.9 dyne

Brookfield viscosity, measured at 20 rpm (± 2 spindle)
and 68% solids: 290 cp

Black Glass

Scattering coefficient at 457 nm: 67 m²/kg
Scattering coefficient at 577 nm: 43 m²/kg
gloss 71%

While the good high shear viscosity characteristics of this commercially available pigment, marketed as a delaminated pigment, will be perceived as advantageous, the comparatively low black glass scatter coefficients will be perceived by the papermakers as a reduction in paper and print quality, particularly in lightweight papers.

Products of the invention possessing the characteristics set forth in the accompanying claims have been made by various techniques, all involving the step of mechanically delaminating kaolin crudes or fractions of crudes, e.g. from the Rio Capim river basin, Para State, Brazil. The Rio Capim kaolins are contained within an extensive sedimentary formation containing coarse and fine sands, clays and silts. The near-surface clay bearing members have been preserved from erosion in plateau tops. The clay members appear to be

- 12 -

stratigraphically flat-lying, with high brightness kaolin horizons occurring underneath variously superficial laterites, sands, and discolored kaolins not suitable for processing. Underneath this waste material, typically there is an horizon of high brightness, low sand content kaolin which is an acceptable source material for products of the invention. In the northern portions of the Rio Capim kaolin district, in the vicinity of Igarape Cipoteua, the crudes can be described as coarse, with the -325 mesh [U.S. sieve] fraction typically having a cumulative particle size distribution of:

	<u>Weight percent finer than</u>	<u>Range</u>	<u>Average</u>
15	2.0 micrometers	72-39%	58%
	1.0 micrometers	55-25%	40%
	0.5 micrometers	34- 8%	20%
	0.2 micrometers	13- 1%	6%

Further to the south, in the vicinity of Igarape Cupijo, the -325 mesh fraction of the crude kaolin is typically finer, averaging 75% finer than two micrometers and 60% finer than one micrometer.

Those skilled in the art know that the use of sedimentation to determine particle size of the thin platelets of mechanically delaminated kaolins results in values that do not truly reflect the size of thin flat plates. Inspection of micrographs (SEM) of the degritt -325 mesh crudes used in the practice of this invention indicate that, numerically, most of the discrete kaolin particles consist of crystals having 1 to 2 micrometers face diameter and less than .5 micrometers edge thickness. Those skilled in the art refer to particles of this size and crystal form as platelets. Typically

- 13 -

the platelets in a suitable crude will have at least one well-formed straight edge, and occasional crystals will have six well-formed edges in a pseudo-hexagonal crystal habit. The coarseness of kaolin particle population is imparted by the kaolin crystals referred by those skilled to in the art as books and large plates. Books are stacks of kaolinite layers. In well-formed crystals the perfect, regular basal cleavage of kaolinite with straight edges at 60 degree angles are readily apparent. Typically the books in crudes used in practice of the invention can be described as roughly equant, on the order of 15 micrometers by 15 micrometers in size. Occasionally, books will develop the vermiform habit wherein the dimension perpendicular to the basal cleavage will be upwards of 40 micrometers in length, often curving at one end of the crystal. Another crystal habit is known as the plate wherein the face diameter is 10 to 15 micrometers and the thickness (the direction perpendicular to the basal cleavage) is on the order of 0.5 micrometers. Plates typically will have less well-formed edges than books.

In the Rio Capim, the degrittied kaolin crudes from the "coarser" northern portion of the area appear to have a greater proportion of books and plates relative to platelets than in the "finer" southern area.

Typically the crude is initially crushed and then blunged in water, preferably containing a clay dispersant, such as, for example, a mixture of soda ash and sodium silicate, or a condensed phosphate salt, e.g., tetrasodium pyrophosphate or sodium polyacrylate. Generally, solids of the blunged clay are in the range of 30% to 65%, usually about 40% by weight. The blunged clay is then degrittied by known means such as the use of

- 14 -

5 screens or gravity settling to remove oversize (grit). Suitable for this purpose are 200 or 325 mesh U.S. Standard (0.074 and 0.044 mm) screens.

10 In an embodiment of the invention, the degrittied slip of kaolin is then separated into one or more coarse and fine size fractions, the finer fraction being, for example, 70 to 90% by weight finer than 2 micrometers. Continuous centrifuges such as those equipped with nozzle bowls or scrolls can be used or gravity settling can be employed for fractionation. Excellent results were obtained with the crude used in an illustrative example by operating the centrifuge to remove and then isolate a fine size fraction of which about 90% by weight of the particles were finer than 2 micrometers and a coarse fraction which was about 25% by weight finer than 2 micrometers. The coarse size fraction remaining after centrifugation to separate the fines is employed as delaminator feed optionally along with a portion of the fines separated during centrifugation and/or a portion of degrittied feed. When a fine fraction is separated in the first classification step, the population of particles of the delaminator feed contains of a higher proportion of large kaolin books and plates than occurs in the population of kaolin particles in the kaolin slip prior to classification. Fines and/or feed are included in delaminated feed primarily to control the particle size distribution of the mechanically delaminated product. See Example 2.

25 In another embodiment of the invention, the degrittied slip is subjected to delamination without an intervening particle size classification. This operation is referred to as "whole fraction delamination". See Example 1 and Example 3.

- 15 -

It is preferred in this invention to terminate the delamination when delamination is essentially complete and attrition of finer than 5 micron platelets begins to occur. The onset of undesired attrition may be
5 controlled by determining the increase in the particle size fraction finer than a particular e.s.d. (e.g., 5.0 and 2.0 micrometers). Duration and intensity of delamination varies, depending on the source of crude, the blend of coarse and fine particle fractions in the
10 delaminator feed, and the desired particle size distribution of the product.

The process of delaminating the clay can be practiced using fine milling media in a batch operation but is advantageously carried out in a continuous manner.
15 Nonlimiting examples of milling media are small ceramic balls, coarse sand, plastic cylinders, beads, or pellets of nylon, styrene-divinyl benzene copolymer, polyethylene or other plastic. The medium acts upon a suspension of the clay in water.

20 Most preferably, the milling medium is minus 20 plus 50 mesh (US sieve) styrene divinyl benzene copolymer beads. Generally the volume of beads to clay slurry varies between 20-70%, most preferably between 35% and 50%. The clay feed to the process should typically be
25 controlled between 20% to 50% solids; however, optimum processing conditions are often achieved between 35 and 45% solids.

A suitable vessel used for the process contains vertical baffles and typically has a height to diameter
30 ratio greater than 1.0 and optimally 1.5 to 2.0. Such a vessel is equipped with an agitation system containing multiple agitator elements attached to a vertical shaft. The number and spacing of the agitators must be optimized

- 16 -

for the specific process conditions in order to impart the necessary combined shear and percussive and frictional energy input necessary to overcome the Van der Waals forces holding individual platelets in a stacked array. Energy input required for delamination will vary
5 due to differences between crudes, process conditions, and equipment; typically requiring 10 to 50 horsepower-hour per ton of clay charged to the delaminators.

In continuous delamination, the clay is fed
10 continuously into a delaminating apparatus and the discharge from the apparatus is advantageously combined with a fractionation of the clay, returning the coarser clay to the apparatus while removing only the finer clay of the desired particle size. The selective takeoff of
15 finer clay, while returning the coarser clay to the vessel in which the delamination is taking place, has the advantage that the overall process yield can be improved and plates greater than 5 micrometers face diameter can be fractured to meet the desired particle size
20 attributes. In this manner, the clay remaining in the apparatus during the continued operation is made up mainly of the coarser clay particles which are undergoing delamination and which are continuously freed from finer clay particles by the selective draw-off and fractionation
25 and return of coarser clay particles.

In this continuous withdrawal of clay suspension, separation of finer clay and return of coarser clay to the apparatus is also advantageously continuous, and can be accomplished by subjecting the withdrawn clay to a
30 centrifugal separation with return of the coarser clay to the apparatus, or by the use of one or more cyclone separators which will separate the finer clay fraction and return the coarser clay to the apparatus.

- 17 -

The slip of delaminated clay is then optionally centrifuged to remove oversize, e.g. particles larger than 2 micrometers, as an underflow and the overflow product is then passed through a high intensity magnetic separator, followed by bleaching, filtration and drying to produce product of the invention. The centrifuged underflow containing oversize may be blended with appropriate levels of delaminated and/or undelaminated clay to achieve blends of desired particle size distribution and further processed in a conventional manner, e.g. magnetic purification and/or bleaching, to produce other advantageous kaolin products.

The fine particle size fraction separated from the coarser kaolin in the first classification step (prior to delamination) may be processed in a conventional manner, e.g., magnetic purification and/or bleaching, to produce No. 1 or No. 2 grade coating clays.

As mentioned, it is within the scope of the invention to delaminate the degrittied slip without first fractionating the slip. It is also within the scope of the invention to delaminate with grinding media other than plastic beads, e.g., by sand, zircon or glass beads or by the delamination process known as "superstrusion".

Delaminated kaolin pigments of the invention can be advantageously used as the single pigment in coating color formulations used to coat paper and paper board. However, it is also within the scope of the invention to employ pigments of the invention in blends with other kaolin and non-kaolin pigments, and to use the blends to coat paper and paperboard. Such blends may be produced prior to the preparation of coating color formulations or produced concomitant with the preparation of coating color formulations.

- 18 -

Delaminated pigments are particularly advantageous when used as the single pigment to coat ground wood-containing lightweight paper. A typical ground wood containing lightweight paper basestock, suitable for coating, may have the following characteristics:

Basis weight: 24 lbs/3300 ft² or 36 g/m²
Brightness: 67.5%
Opacity: 76%

In preparing coating color formulations, coating pigments are admixed in a conventional manner with other constituents and binders, materials that bind the coating pigments to the paper basestock surface. Coating color formulations will vary from mill to mill for the same end- use application, and will differ on the basis of the surface characteristics required by different printing methods commonly used. For example:

Typical Light Weight Coated Paper - Coating Formulations

20

Europe

Offset Paper

100 pts pigment

10 pts Dow 685

5 pts PG280

0.5 pts Nopcote^R C-104

0.5 pts Sunrez^R 700C

Rotogravure Paper

100 pts pigment

4.8 pts Acronal³ 548

0.5 pts Nopcote³ C-104

25

30

- 19 -

United StatesOffset PaperRoto Gravure Paper

100 pts pigment

100 pts pigment

8 pts PG280

7 pts PG280

5

8 pts CP640 A

4 pts CP620 A

0.5 pts Nopcote[®] C-1045 pts Nopcote[®] C-1040.5 pts Sunrez[®] 700C

pts = parts

10 All particle sizes used in the specification and claims are determined with the SEDIGRAPH 5100 particle size analyzer and are reported as equivalent spherical diameters (e.s.d.) on a weight percentage basis.

15 Light scattering and gloss were determined by coating the kaolin clay suspensions at 60% solids onto black glass plates at a coat weight of 7.0 - 14.0 g/m² (expressed as dry clay). The reflectance of the coatings, after drying in air, is measured at wavelengths 457 nm and 577 nm by means of an Elrepho reflectometer.

20 The 457 nm wavelength corresponds to the wavelength used in the TAPPI brightness measurement and the 577 nm wavelength to that used to measure opacity. The reflectance values are converted by the use of Kubelka-Munk equations to light scattering values (m²/Kg). The

25 light scattering values are a measure of the opacity potential of the clay. The higher values indicate that light, rather than passing through, is reflected and scattered back. The higher the light scattering value, the higher the opacity potential of the clay. The black

30 glass gloss value is a measure of specular gloss at 75 degrees (15 degrees from the plane of the paper), and is widely used as a particle measure of surface quality and shiny appearance (which is conventionally equated with

- 20 -

high quality). In many applications, high gloss values are desirable.

In preparing slurries for measurement of high shear (Hercules) and low shear (Brookfield) viscosity, Engelhard Corporation procedure PL-1 was used. Brookfield viscosity was measured using TAPPI procedure T648 om-88 at 20 rpm using the #1 or #2 spindle; in some cases Brookfield viscosity was measured at 100 rpm using the #3 spindle. All slurries were formulated with optimum amount of dispersant, following the PL-3 procedure of Engelhard Corporation. Descriptions of PL-1, PL-3 and Hercules viscosity measurement procedures appear in U.S. 4,738,726.

In the examples which follow, references are made to pigment brightness, which was determined in the conventional manner (TAPPI standard T452 m - 58) using a G.E. Brightness meter.

In Examples 1 & 2 which follow, the kaolin clay crudes were obtained from deposits of the northern portion of the Rio Capim river basin of Para, Brazil. In Example 3, the kaolin crudes were a bulk sample obtained from deposits approximately 75 kilometers due north of Manaus, Amazonas, Brazil.

- 21 -

EXAMPLE 1

Whole Fraction Delaminated Products

5 This example demonstrates the embodiment of the invention in which a degrittied slip of kaolin is subjected to mechanical delamination without first fractionating the slip (whole fraction delamination). The kaolin slip used as feed in the process was a sample of Capim kaolin, described above. The slip was prepared
10 by blunging kaolin crude (pH 4.4) in water containing sodium polyacrylate (C211 brand) and soda ash as a dispersant, resulting in a slurry having a pH of 8.2. The slip was degrittied in two stages, the first involving allowing the slip to remain quiescent (settle) for 5
15 minutes and then passing the nonsettled portion through a 200 mesh screen. The degrittied slip at about 39% solids contained about 86% of the starting crude. Particle size of the recovered kaolin was 54% finer than 2 micrometers. Brightness was 81.3%; TiO_2 and Fe_2O_3 were 1.08% and 0.71%,
20 respectively.

Delamination was carried out in a pilot plant delamination simulator which consists of a stainless steel vessel nominally 10" ID by 15" high. Within the vessel are three vertical baffles approximately 1/2" wide
25 extending the length of the vessel. The agitation system utilizes three ceramic cones mounted in a turban array where two or more cones can be mounted on the vertical shaft. The power for the vessel is provided by a 3/4 HP drill press with variable speed control. In this vessel,
30 approximately 2.5 gallons of clay slip are delaminated per batch utilizing the necessary bead volume ratio of styrene divinyl benzene copolymer to achieve optimum results. In this example, bead volume was 50% and

- 22 -

residence time of the slip in the delaminator was 55 minutes. Bead size was minus 20 plus 50 mesh (US sieve), and shape was spherical.

Particle size of the delaminated product was about 70% finer than 2 micrometers. Brightness was 81.9%. TiO_2 and Fe_2O_3 analyses were 1.08 and 0.72%, respectively, indicating that kaolin was not brightened during delamination. Solids of the delaminator discharge was 19.2%.

In one case the delaminator discharge was then charged to brightness enhancing equipment, described below, resulting in a finished Product A with 70% of the kaolin particles finer than 2 micrometers. In another case, the delaminator discharge was charged to a Sharples centrifuge which divided the slip into Product B, a fine fraction of 80% finer than two micrometers (77.3% yield and 19.2% solids), and a coarse reject fraction.

For both products A and B, the delaminated kaolin was then charged to a conventional high intensity magnetic separator using various throughput rates in order to remove colored paramagnetic impurities and thereby improve brightness. Prior to magnetic treatment the brightness of the feed kaolin was 82.3%; TiO_2 and Fe_2O_3 were 1.13 and 0.70%, respectively. The pilot plant High Intensity Magnetic Separator is fitted with a 1" ID x 20" high canister containing approximately 100 pads of 430 stainless steel. Space velocity calculations are utilized to simulate equivalent processing conditions for commercial scale HIMS units. Typically, commercial scale units have canisters of 84 or 120 inch diameter x 20 inch high matrix. An important consideration in plant scale-up is the performance of a process under varying capacities. Thus, in order to simulate future scale - up

- 23 -

requirements space velocities are varied typically to simulate production capacities of 20 to 40 tons per hour utilizing an 84" HIMS unit. At throughput rates between 20 and 40 tons per hour, products having brightness in the range of 87.7 to 88.4% were produced. Those skilled in the art will recognize that the 5 - 6 points increase in brightness as a result of magnetic separation treatment was unusually high; typical Georgia kaolins experience an increase in brightness of only 1 to 3 points by treatment in conventional high intensity separators.

Brightness of all magnetically purified products was further significantly increased by floccing the slip of magnetically purified kaolin with 6#/T aluminum sulfate (4.7 pH), treatment with a conventional sodium dithionite bleach reagent, followed by filtration and viscosity measurement. Brightness results for runs at various magnet throughput rates and bleach levels are reported below in table form for the 80% finer than two micrometer product. (The 70% finer than two micrometers product responded similarly)

Brightness of Delaminated Beneficiated Kaolin Products

Bleach #/T	Magnetic Through-Put tons/hour			
	0 t/hr	20 t/hr	30 t/hr	40 t/hr
0	82.3	88.4	87.8	87.8
7	84.2	89.6	89.4	88.8
10	85.0	89.6	89.4	89.1
13	84.7	89.6	89.5	89.2

- 24 -

The characteristics of the two products A and B of this example:

	<u>Particle Size</u>	<u>A</u>	<u>B</u>
5	% finer than 10 micrometers	98	100
	% finer than 5 micrometers	92	98
	% finer than 2 micrometers	72	80
	% finer than 1 micrometers	52	60
	% finer than 0.5 micrometers	28	32
10	% finer than 0.2 micrometers	7	6
	Median Particle Size	.94	.77
	Ratio: $\frac{\% \text{ finer than } 2.0}{\% \text{ finer than } 0.5} =$	2.57	2.50
15	<u>Surface Area</u> m ² /g	10.6	11.5
	<u>Viscosity</u>	<u>A</u>	<u>B</u>
20	Solids%	67.0	67.0
	Brookfield #2 @ 20 rpm	97 cp	76 cp
	@ 100 rpm	77 cp	71 cp
	Hercules @ 1100 rpm	5 dynes	5.2 dynes
25			

- 25 -

Example I - Whole Delaminated Products Continued

Products of the invention, A and B, and two commercially available high aspect ratio delaminated kaolin products C and D, made from Georgia, USA and Cornwall, United Kingdom kaolin crudes, respectively, were admixed in a conventional manner with binders, commonly used in Europe for rotogravure paper in the following formulation:

Coating Formulation

	Pigment	100
10	Acronal 548	4.8
	Nopcote C-104	0.5

The admixtures, commonly referred to as coating colors, were tested for viscosity in a conventional manner:

	<u>Product</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
15	Solids (%)	59.4	59.2	59.2	55.6
	pH	9.5	9.6	9.5	9.8
	Brookfield (cps)				
	20 rpm	2070	2140	3510	7220
	100 rpm	672	678	1064	2176
20	Spindle	#4	#4	#4	#5
	4400 H.E.P. "E"	20.4	22.4	25.0	19.6

Note that commercially available product D has substantially worse rheology as it is measurable in this formulation at 3.5% lower solids than products of the invention A and B and commercially available product C. At the same solids level, products of the invention A and B have superior viscosity to commercially available product C.

The coating color was then applied to a European base sheet suitable for rotogravure printing applications. The following coated sheet and print properties were measured:

- 26 -

EUROPEAN LWC ROTOGRAVURE
Coated Sheet Properties

	<u>Product</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	Brightness (%)	74.0	74.2	73.6	73.6
5	Opacity (%)	86.3	86.5	85.8	85.5
	Gloss (%)	49	54	48	43
	Heliotest (mm)				
	@ 25 Kg/f	22	25	19	18
	@ 30 Kg/f	48	67	52	42
10	PPS	1.19	1.10	1.28	1.27

Properties shown at 5.5 lb/3300 ft²
Calendar Conditions: 1 nip at 2000 psig and 140°C

- 15 In each of these measures of desirable coated sheet optical properties and printability, the products of the invention A and B are equivalent to or superior to the commercially available products C and D.

Samples of product A, B, C, D as described above were admixed with binders typically used in European LWC formulations:

Coating Formulation

20	Pigment	100
	Dow 685	10
	PG 280	5
	Nopcote C-104	0.5
	Sunrez 700C	0.5

- 25 viscosity measurements of the four coating colors were then taken in a conventional manner with the following result:

- 27 -

EUROPEAN LWC OFFSET
Coating Color Properties

	<u>Product</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	Solids (%)	58.1	58.1	58.0	58.3
5	pH	8.5	8.5	8.5	8.5
	Brookfield (cp)				
	20 rpm	840	940	1490	2100
	100 rpm	320	330	534	760
	Spindle	#4	#4	#4	#4
10	4400 H.E.P. "E"	15.0	15.2	24.8	26.0

The coating color formulations A, B, C, D were applied to a European base sheet suitable for light weight coated offset applications. Coated sheet and print properties were measured in conventional manner with the following results:

15	EUROPEAN LWC OFFSET Coated Sheet Properties				
	<u>Product</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	Brightness (%)	71.4	71.7	70.9	70.9
	Opacity (%)	81.6	81.6	80.7	80.6
20	Gloss (%)	55	59	56	49
	Print Gloss (%) o.d. = 1.6	79	81	79	79
	Print Through Resistance (%) o.d. = 1.6	79	79	79	79
25	IGT pick (vvp)	35	33	32	33
	K&N (%)	21	22	20	18
	PPS	1.13	1.06	1.08	1.16

30 Properties shown are at 5.5 lb/3300 ft²
Calendar conditions: 4 nips, 2000 psi_g, 140°F

Thus, in a European LWC offset application, products of the invention A and B demonstrated better coating color high and low shear viscosities than commercially available products C and D, and have equivalent to slightly superior optical and printability characteristics.

EXAMPLE 2**Delaminated Products From Coarse Particle Size
Fractions Of Crude**

5

This example illustrates the production of a mechanically delaminated clay product of the invention from a coarse particle size fraction of crude and a by-product No. 1 grade product.

10

The crude was blunged in water at 40% solids, resulting in a pH of 4.4. To facilitate subsequent processing the slurry was dispersed by adding soda ash (2 pounds per ton) and N² Brand sodium silicate solution (4 pounds per ton), resulting in a pH of 8.4.

15

The dispersed slurry was degrittied by allowing it to settle for 5 minutes and then passing the nonsedimented portion through a 200 mesh screen (U.S. Standard) to remove grit. The size of the kaolin in the minus 200 mesh (degrittied) slip was 54% by weight finer than 2 micrometers. Brightness was 82.6%. Chemical analysis was 0.90 weight % TiO₂ and 0.58% Fe₂O₃.

20

The degrittied slip at 32.7% solids was then divided in a Sharples centrifuge into a fine fraction (93% finer than 2 micrometers at 20.6% solids) and a coarse fraction (22% finer than 2 micrometers).

25

To the coarse centrifuge underflow fraction (22% finer than 2 micrometers) there was added a portion of the fines (93% finer than 2 micrometers) and a portion of degrittied feed (54% finer than 2 micrometers) to produce a delaminator charge have a desired particle size of about 51% minus 2 micrometers. The blend of clays charged to the delaminator had a brightness of 82.8% and

30

- 30 -

analyzed 0.90% TiO_2 and 0.63% Fe_2O_3 .

5 The resulting blend of dispersed clays at 42.6% solids was then subjected to mechanical delamination in a pilot plant delamination simulator, described in the previous example, in a batch operation for 1-1/2 hours using minus 20 plus 50 mesh spherical styrene - divinyl benzene co-polymer beads; bead volume was 35% during delamination. Particle size distribution of the
10 delaminated product was 62% by weight finer than 2 micrometers; TiO_2 and Fe_2O_3 contents were 0.86% and 0.64%. Brightness was 83.5%.

The slurry discharged from the delaminator, which had a distinctly pink appearance, was then separated in a
15 Sharples centrifuge, recovering a delaminated fractionated product having No. 2 coating clay particle size specification (81% finer than 2 micrometers) and 84.1% brightness. TiO_2 was 1.24%; Fe_2O_3 was 0.61%. The delaminated product was then purified in a high intensity
20 magnetic separator with a 430 stainless steel wool matrix. As a consequence of magnetic separation, the distinctly pink color disappeared.

Portions of the mechanically delaminated, magnetically purified clay were then bleached with
25 various amounts of sodium dithionite. Optimum bleach dosage was 12 pounds per ton, resulting in a bleached, delaminated product having a brightness of 90.2%. TiO_2 content was 0.78%; Fe_2O_3 was 0.56%.

The 93% finer than 2 micrometer fraction of
30 undelaminated clay from the initial Sharples classification (prior to delamination) was also magnetically purified, bleached and spray dried to recover a No. 1 coating clay.

- 31 -

The delaminated product made in the above described procedure had the following characteristics:

5 Particle Size:

	% finer than 10.0 micrometers	>99
	% finer than 5.0 micrometers	99
	% finer than 2.0 micrometers	81
	% finer than 1.0 micrometers	56
10	% finer than 0.5 micrometers	26
	% finer than 0.2 micrometers	3

Median Particle Size: 0.38 micrometers

15 Ratio: $\frac{\% \text{ finer than } 2.0 \text{ micrometers}}{\% \text{ finer than } 0.5 \text{ micrometers}} = 3.1$

Surface Area: 9.4 m²/g

20 Slurry Viscosity

At 68.5% solids:

Brookfield @ 20 rpm: 80 cp
 @ 100 rpm: 70 cp
 Hercules @ 1100 rpm: 6.4 dyne-end point

25 At 71.7% solids:

Brookfield @ 20 rpm: 170 cp
 @ 100 rpm: 132 cp
 Hercules: 245 rpm @ 16 dynes

30

Black Glass

Scattering co-efficient at 457 nm: 113 m²/Kg
 Scattering co-efficient at 577 nm: 81 m²/Kg
 Gloss 82.5%

35

It is within the scope of the invention to utilize feed to the delaminator which consists of coarse centrifuge underflow fraction (about 20% finer than 2 micrometers) and a portion of degritt feed (about 55%

40

finer than two micrometers) to produce a delaminator
charge of a desired particle size of about 35% minus 2
micrometers. The resulting blend of dispersed clays is
then subjected to mechanical delamination under the
5 conditions and in the manner described above. The
delaminator discharge has a particle size distribution of
about 60% finer than two micrometers. The slurry
discharge is then charged to a Sharples centrifuge,
recovering a delaminated fractionated product stream with
10 a particle size of about 80% finer than 2 micrometers,
which is then purified as described above. The
characteristics of the delaminated, fractionated product
conform to the specifications of the products of the
invention. This embodiment of the invention is not
15 limited to the specific particle size variations set forth
above.

- 33 -

Delaminated Products from Coarse Particle Size Fractions of Crude

- Delaminated product from the above described procedure was admixed with binders and other constituents in the formulation described below to make paper coating colors which were tested for coating color viscosity and then applied in a conventional manner to appropriate commercially available European and American lightweight paper base stock.

Formulations used are:

Coating Color Formulations

10	<u>American LWC Offset</u>		<u>American LWC Roto</u>		<u>European LWC Roto</u>	
	Pigment	100	Pigment	100	Pigment	100
	PG 280	8	PG 280	7	Resyn 6833	5
	CP 640A	8	CP 620A	4	FinnFix 5	1.5
	Sunrez 700C	0.5				
15	Nopcote C-104	0.5	Nopcote C-104	0.5	Nopcote C-104	0.5

The pigments tested included:

- Pigment A - Product of the invention as described in this example.
- 20 Pigment C - Commercially available mechanically delaminated pigment made from Georgia, USA kaolins.
- Pigment D - Commercially available naturally delaminated pigment made from kaolins mined in Cornwall, United Kingdom.

American LWC Roto

- 25 Coating color viscosity and coated sheet properties were measured as follows:

	<u>Product A</u>	<u>Product C</u>
Solids (%)	57.1	57.0
pH	8	8
30 Brookfield (cp)		
20 rpm	2640	2800
100 rpm	900	978
4400 H.E.P. 'E'	18.2	13.6

COATED SHEET PROPERTIES
(American LWC Roto)

	<u>Product A</u>	<u>Product C</u>
	55	49
5 Gloss (%)		
	74.2	73.4
Brightness (%)		
	85.2	84.6
Opacity (%)		
	84	69
Heliotest (mm)		

Properties shown are at 5.5 lb/3300 ft²
Calendar conditions: 3 nips, 2000 psig, 140°F

10 European LWC Rotogravure

Similarly, coating color viscosity and coated sheet properties for Product A, Product C, Product D were tested in the European LWC rotogravure formulation with the following results:

	<u>COLOR PROPERTIES</u> (European LWC Roto)		
	<u>A</u>	<u>C</u>	<u>D</u>
15 Solids (%)	57.1	57.0	57.2
pH (NaOH)	8	8	8
20 Brookfield (cps)			
20 rpm	1,050	1,680	13,150
100 rpm	352	536	4,280
4400 H.E.P. 'E'	16.0	22.8	35.6

- 35 -

COATED SHEET PROPERTIES
(European LWC Roto)

	<u>A</u>	<u>C</u>	<u>D</u>
Gloss (%)	53	46	43
5 Brightness(%)	74.8	73.8	74.2
Opacity (%)	85.6	84.5	84.5
Hellotest (mm)	51	40	52

Properties shown are at 5.5 lb/3300 ft²
Calendar conditions: 2 nips, 1600 psig, 140°F

- 10 In each of the cases above, the product A of the invention provided equivalent to superior to significantly superior optical and printability characteristics compared to commercial delaminated pigments C and D; and the product of the invention had
15 significantly lower high and low viscosity than the commercially available pigments at the same solids level in the same coating color formulation.

- An alternative means of quantifying the novel, unexpected viscosity characteristics of the delaminated
20 product of the invention is to determine the coating color solids level at which the product of the invention will report viscosity measurement values equal to the commercially available pigments. This determination was made by measuring the Brookfield and
25 Hercules viscosity of the commercially available Product C at typical color coating solids level 57%.

- 35A -

A product of the invention, Product A, was admixed in a pigment binder system at a significantly higher solids level than 57% solids and viscosity measurements were taken; then the solids level was reduced by one percent
5 increments with the addition of deionized water, with viscosity measurements again taken at each new lower solids level. This process is repeated to establish a range of data relating coating color solids to viscosity and until the viscosity measurements of
10 product A, initially higher than that of product C, are, via dilution of solids content, lower than the viscosity measurement of product C.

In this manner and with the pigments of this example, it was determined that product of the invention A can
15 be dispersed in an American LWC offset formulation and achieve an equivalent Brookfield viscosity value to commercially available product C at 2% higher color solids level and an equivalent Hercules viscosity value at 3% higher coating color solids. These differences
20 are significant and can provide substantial commercial advantages to the paper maker.

- 36 -

EXAMPLE 3

Whole Fraction Delamination
(Manaus, Amazonas, Brazil kaolin crudes)

5

In this example, processing steps described above in Example 1 for Product A were employed for crudes from deposits of kaolinitic sands located about 75 kilometers north of the city of Manaus, Amazonas state, Brazil.

10

The slip was prepared by blunging the kaolin crude in water containing Calgon[®] dispersant, resulting in a slurry with a pH of 7.1. The slip was degritt in two stages, the first involving allowing the slip to remain quiescent for about 5 minutes and then passing the nonsettled portion through a 200 mesh screen (U.S. standard). The degritt slip at about 41% solids contains about 43% of the starting crude. Particle size of the recovered kaolin was 57% finer than 2 micrometers. Brightness was 82.6%; Fe₂O₃ and TiO₂ were 0.69% and 0.81% respectively.

15

20

Delamination was carried out in a pilot plant delamination simulator as described above. Bead volume was 50% and residence time was 45 minutes. The discharge of the delaminator was charged to a magnetic separator and then flocced and bleached with 6#/ton K-brite[®] sodium dithionite solution, then filtered, rinsed and dried using conventional procedures.

25

30

- 37 -

The delaminated pigment product of this example had the following characteristics:

	<u>Particle Size</u>	99% finer than 10 micrometers
5	<u>Distribution</u>	93% finer than 5.0 micrometers
	(weight % finer	71% finer than 2.0 micrometers
	than e.s.d.)	49% finer than 1.0 micrometer
		27% finer than 0.5 micrometers
10		3% finer than 0.2 micrometers
	Median particle size:	1.02 micrometers
	Ratio:	$\frac{\% \text{ finer than } 2.0 \text{ micrometers}}{\% \text{ finer than } 0.5 \text{ micrometers}} = 2.6$
15	<u>Surface Area:</u>	9.2 m ² /g
	<u>Viscosity</u> , measured at 70.3% solids	
	Brookfield @ 20 rpm:	100 cp
20	@ 100 rpm:	80 cp
	Hercules @1100 rpm:	7.7 dynes
	<u>Black Glass</u>	
25	Scatter coefficient at 457 nm:	108 m ² /Kg
	Scatter coefficient at 577 nm:	82 m ² /Kg
	Gloss:	not measured

- 38 -

Example 4 - Processing replicates of novel whole fraction delaminated and delaminated products from coarse fractions of crude.

- 5 In this example, the crudes used in Example 1 and Example 2 were again processed, in part, in a manner more fully described in Example 1 and Example 2 to make products of the invention.

Whole Fraction Delamination

- 10 In this case a degrittied slip of kaolin, with physical characteristics as reported below, is subjected to mechanical delamination without first fractioning the slip. The delaminator discharge, with physical characteristics as described below, was charged to a Sharples centrifuge which divided the slip into Product A, a fine fraction of 75% finer than two micrometers, as
15 more fully described below, and a coarse reject fraction. The product slip can then be subjected to brightness enhancement as described in Example 1.

Whole Fraction Delaminated

	Degrittied Crude & Delaminator Charge	Delaminator Discharge	Final Product
20			
<u>Particle Size Distribution</u>			
% less than 5 microns	76.4	91.1	95.8
2 microns	55.0	67.6	74.5
1 micron	40.4	47.4	53.2
.5 micron	23.3	26.1	28.6
.3 micron	10.3	9.2	11.4
.2 micron	4.8	3.6	4.4
<u>Surface Area</u> m ² /g	7.8	7.9	8.9
BET - N ₂			
<u>Viscosity</u>			
<u>72% Solids</u>			
Brookfield @ 20 RPM	90 cps	138 cps	205 cps
Brookfield @ 100 RPM	122 cps	168 cps	174 cps
<u>68% Solids</u>			
Brookfield @ 20 RPM	40 cps	59 cps	64 cps
Brookfield @ 100 RPM	71 cps	78 cps	76 cps
Hercules @ 1100 RPM	1.9 dynes	2.3 dynes	2.0 dynes
Hercules @ 4400 RPM	12 dynes	28.8 dynes	26.8 dynes

Delaminated Product from Coarse Fraction of Crude

In this example, the degrittied kaolin crude slip, with physical characteristics as described below, is separated by a centrifuge, as described in Example 2, into a fine fraction and coarse fraction with particle size distributions as described below. A portion of the fine fraction recovered in the first step is then admixed with the coarse fraction in order to make a kaolin slip for charge to the delaminator; the portion of fine fraction remaining can be further processed in a conventional manner into a fine fraction No. 1 grade product, if desired. The delaminator charge, with physical characteristics as described below, is charged to the delaminator, as described in Example 2. The delaminator discharge with physical characteristics as described below is then charged to a centrifuge to separate the slip into a delaminated product as described below, and a coarse reject fraction. The fractionated, delaminated product slip can then be subjected to brightness enhancement, as described in Example 2.

- 40 -

Degritted Crude & Centrifuge Charge	Fine Fractionated Slip	Coarse Fraction	Delam. Charge	Delam. Discharge	Centrifuge Product
--	------------------------------	--------------------	------------------	---------------------	-----------------------

Particle Size Distribution

3 less than 5 microns	76.4	59.9	73.3	89.5	97.5
2 microns	55.0	28.3	49.9	63.0	75.3
1 micron	40.4	19.1	35.3	42.8	52.7
.5 micron	23.3	11.1	21.4	23.2	28.5
.3 micron	10.3	6.0	8.8	9.8	11.1
.2 micron	4.8	2.6	3.1	4.7	3.6

Surface Area m²/gDET - H₂

7.8

8.3

8.7

Viscosity721 Solids

Brookfield @ 20 RPM	90 cps	90 cps	112 cps	158 cps
Brookfield @ 100 RPM	122 cps	129 cps	143 cps	170 cps

681 Solids

Brookfield @ 20 RPM	40 cps	41 cps	42 cps	61 cps
Brookfield @ 100 RPM	71 cps	76 cps	66 cps	73 cps
Hercules @ 1100 RPM	1.9 dynes	2.6 dynes	2.6 dynes	2.5 dynes
Hercules @ 4400 RPM	12 dynes	15.2 dynes	28.4 dynes	32.0 dynes

CLAIMS:

1. A paper coating pigment comprising delaminated hydrous kaolin particles having the following characteristics:

(1) Particle Size (e.s.d. as determined by Sedigraph)

(a) At least 95% finer than 10 micrometers
37% or less finer than 0.5 micrometers
12% or less finer than 0.2 micrometers

(b) Median particle size: at least 0.70 micrometers

(c) ratio $\frac{\% \text{ finer than } 2 \text{ micrometers}}{\% \text{ finer than } 0.5 \text{ micrometers}} : > 2.0$

(2) Surface area: 12.5 m²/gm or less (BET method using N₂ as adsorbate)

(3) Viscosity

(a) Brookfield viscosity, measured at 20 rpm and 67-68% solids: 175 cp or less

(b) Hercules viscosity, measured at 1100 rpm and 67-68% solids: dyne endpoint.

(4) Black glass scatter

scatter coefficient at 456 nm: $\geq 100 \text{ m}^2/\text{Kg}$
scatter coefficient at 577 nm: $\geq 80 \text{ m}^2/\text{Kg}$

- 42 -

2. A pigment according to claim 1 having a gloss (black glass) of at least 75%.

3. A pigment according to claim 1 or 2 having a Brookfield viscosity, measured at 20 rpm and at 100 rpm at 72% solids, of 300 cp or less.

4. An aqueous slurry containing pigment according to claim 1 or 2 or 3.

5. An aqueous paper coating composition containing pigment according to claim 1 or 2 or 3 and organic binder.

6. A paper web coated with pigment according to claim 1 or 2 or 3.

7. A method of making a hydrous kaolin pigment which comprises

(A) providing degrittet -325 mesh kaolin crude having the following characteristics:

(1) Particle Size (e.s.d. as determined by Sedigraph)

(a) % less than 2 microns: 40 - 65%
% less than 0.2 microns : \leq 12%

(b) ratio % less than 2 microns : $>$ 2.1
% less than 0.5 microns

(2) Surface Area: 12.0 m²/gm or less (BET method using N₂ as adsorbate).

(3) Structural Order

(a) Hinckley Index: > 0.90

(b) C-axis crystal coherence - Full-Width-Half-Maximum
measure of (001) peaks -
FWHM (001) ≤ 0.26

(4) Cation Exchange Capacity - measured by Na^+ adsorption at pH 4.0
on non-dispersed minus 325 mesh crude: ≤ 0.05
microequivalents/ m^2 ; and

(B) subjecting the crude to delamination and terminating
delamination when a predominant proportion of the original booklet
particles have been parted along basal (001) cleavages into
discrete platelets but before significant attrition of platelets
occurs.

8. A method according to claim 7 wherein the delamination is
terminated when (a) the rate of change in particle size
distribution at predetermined particle size control points
approaches zero, and/or (b) an increase in the percentage of very
fine particles (less than .3 microns) is noted.

9. A process for making a hydrous kaolin pigment which
comprises

(A) providing degrittied -325 mesh kaolin crude having the
following characteristics:

(1) Particle Size (e.s.d. as determined by Sedigraph)

(a) % less than 2 microns: 40 - 65%
% less than 0.2 microns : $\leq 12\%$

- 44 -

(b) ratio % less than 2 microns : > 2.1
% less than 0.5 microns

(2) Surface Area: 12.0 m²/gm or less (BET method using N₂ as adsorbate).

5

(3) Structural Order

(a) Hinckley Index: > 0.90

(b) C-axis crystal coherence - Full-Width-Half-Maximum
measure of (001) peaks -
FWHM (001) ≤ 0.26

10

(4) Cation Exchange Capacity - measured by Na⁺ adsorption at pH 4.0
on non-dispersed minus 325 mesh crude: ≤ 0.05
microequivalents/m²; and

(B) subjecting the crude to delamination until there is
formed a delaminated product having the following characteristics:

15

(1) Particle Size (e.s.d. as determined by Sedigraph)

(a) At least 95% finer than 10 micrometers
37% or less finer than 0.5 micrometers
12% or less finer than 0.2 micrometers

(b) Median particle size: at least 0.70 micrometers

20

(c) ratio % finer than 2 micrometers : > 2.0
% finer than 0.5 micrometers

(2) Surface area: 12.5 m²/gm or less (BET method using N₂ as adsorbate)

(3) Viscosity

- (a) Brookfield viscosity, measured at 20 rpm and 67-68% solids: 175 cp or less
- (b) Hercules viscosity, measured at 1100 rpm and 67-68% solids: dyne endpoint.

5

(4) Black glass scatter

scatter coefficient at 456 nm: $\geq 100 \text{ m}^2/\text{Kg}$
scatter coefficient at 577 nm: $\geq 80 \text{ m}^2/\text{Kg}$

10

10. A method according to claim 7, 8 or 9 wherein the content in the kaolin crude of particles of less than 0.2 microns is 5% or below.

INTERNATIONAL SEARCH REPORT

PCT/US92/08462

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C09C 1/28, C09C 3/06

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/688,211

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,943,324 (BUNDY ET AL) 24 JULY 1990 (See col. 1 third paragraph)	1-10
A	US,A, 3,343,973 (BILLUE) 26 SEPTEMBER 1967 (See claims 1-13)	1-10
A	US,A, 4,916,094 (SALINAS) 10 APRIL 1990 (See abstract)	1-10
A	US,A, 3,798,044 (WHITLEY ET AL) 19 MARCH 1974 (See abstract)	1-10

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
* A	document defining the general state of the art which is not considered to be part of particular relevance		
* E	earlier document published on or after the international filing date	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* O	document referring to an oral disclosure, use, exhibition or other means		
* P	document published prior to the international filing date but later than the priority date claimed	* G	document member of the same patent family

Date of the actual completion of the international search

16 OCTOBER 1992

Date of mailing of the international search report

04 JAN 1993

 Name and mailing address of the ISA/
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Authorized officer

PAUL MARCANTONI

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-1196

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/08462

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 3,394,022 (LYONS ET AL) 23 JULY 1968 (See claims 1-2)	1-10
A	US,A, 4,820,554 (JONES ET AL) 11 APRIL 1989 (See abstract and claim 1)	1-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/08462

A. CLASSIFICATION OF SUBJECT MATTER: US CL :

106/486,106/416,501/144,501/145,501/146,162/181.8,428/144,428/153428/537.5